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"Substitute Specification"

PROCESS FOR FURTHER PROCESSING OF SMALL GLASS PARTICLES

BACKGROUND OF THE INVENTION

This invention relates to a process for the further processing of small glass particles, for example, in the form of scrap glass granulate with a grain size in the range between 0.3 and 4 mm, or glass beads with diameters in the range between 0.1 and 2.3 mm.

In our current industrial society very large amounts of scrap glass are formed. For environmental reasons, it therefore seems desirable for this scrap glass to be reused.

In this connection it is indeed possible for the scrap glass to be remelted in order to produce, for example, new bottles from it. The disadvantage of remelting scrap glass is due to homogenization and degassing of glass melts with temperatures in the range between 1400°C and 1600°C, which are necessary so that the remelting of scrap glass can only be accomplished with very high energy costs.

Within the framework of re-use of scrap glass, mainly small glass particles in the form of scrap glass granulate and spherical glass beads produced therefrom are available. The grain size of these glass particles can be very accurately set by screening.

The object of this invention is to provide a process with which further processing of these glass particles is possible at relatively low energy cost, using simple technical aids. New products formed can be used for very diverse purposes in industry.

SUMMARY OF THE INVENTION

Glass particles are produced with a relatively low energy cost. The surfaces of the glass particles are brought into contact with a low melting silicate flax or enamel, for example, lead borosilicate, sodium borosilicate, fluoroborosilicate or mixtures thereof, in amounts of 2-9% by weight,

preferably 3-5% by weight. The glass particles are exposed to a heat treatment in the range of 540°C to 800°C, preferably in the range of 560°C to 660°C, at which the low melting silicate flax or enamel melts on the surfaces of the glass particles.

DETAILED DESCRIPTION OF THE INVENTION

Within the framework of the invention, the surfaces of existing glass particles are brought into contact with a low-melting silicate flux or enamel, whereupon at relatively low temperatures around 600°C and accordingly with low power consumption, a heat treatment is done, in which the low melting silicate flux or enamel is melted. Essentially this measure allows three different things.

1. A very economical color coating of the existing glass particles in the case of glass beads or glass granulates.
2. Very economical connection of one layer of glass particles on any carrier layer; in conjunction with flat glass, ceramic tiles, metal surfaces, glass films and/or ceramic fabrics this allows production of highly light reflective surfaces.
3. Very economical joining of glass particles among one another; this allows production of porous glass components, heat insulating glass, cladding panels and the like.

Other details of the invention follow from the following description.

1. Production of a color coating on glass beads or glass granulate

The raw materials used are uncolored glass beads or screened glass granulate, and particles of this type are made available by industry at very low prices. These glass beads have diameters in the range between 0.1 and 2.3 mm, or these glass granulates have a grain size between 0.3 and 4 mm, and are

subsequently wetted with a wetting agent in the form of an easily gasifying screen printing oil, a liquid which contains both boric acid and also fluorine salts, or mixtures thereof. While wetting takes place using the easily gasifying screen printing oil alone, the surface of the glass beads, or glass granulates, is softened by the liquid which contains both boric acid and also fluorine salts with the simultaneous action of heat, so that by suitably adjusting the ratio between the screen printing oil and the liquid which contains both boric acid and also fluorine salts, the thickness of the color coating, to be produced, can be adjusted at will.

Subsequently, the superficially treated glass particles are uniformly coated in a low melting enamel or flux, the color feed thereof, taking place in powder form. In this way a colored layer can be applied to the glass beads, or glass granulates, with the percentage by weight, generally in the range between 2 and 9%, by weight, preferably in the range between 3 and 5%, by weight.

The colored layer applied to the glass particles can now be fired on in two ways. In one case, the coated glass particles are caused to roll off over a slanted plane, consisting of stainless steel sheets, these stainless steel sheets being provided with a boron nitrite coating for protection. In doing so, the rolling glass particles traverse a thermal zone with temperatures in the range between 540°C and 800°C, preferably in the range between 560°C and 660°C; this causes the applied color layer to be fired onto and into the surface of the glass particles.

Alternatively, the glass particles, provided with a colored layer, can be placed in a mold which does not stick to them, for example, a ceramic fiber mold, or a mold consisting of refractory sheets, with a layer thickness of a maximum of 6 cm. The molds filled with the glass particles, are then placed in a furnace, whereupon the colored layer on the glass particles is fired on, and heated in the range between 540°C and 800°C, and

preferably in the range between 560°C and 660°C. In doing so however only spot connections of the glass particles placed in the respective molds among one another arise, which thus after cooling can be very easily pulverized within a corresponding mill, a pulverizing device, or using hard rubber, or hardwood rollers and can be isolated into colored glass particles separate from one another.

Since within the framework of the invention not all the glass particles in the form of glass beads, or glass granulates, are colored, but only a thin outside layer, glass particles colored in this way can be produced at a very low cost, because only relatively small amounts of expensive colored glass additives in the form of rare earths, and the like, are necessary. The described process allows easy, fast and extremely diverse coloring of glass particles, because the most varied color mixtures, as are supplied by companies such as Hereus and Degusa for the ceramic and glass refinement industry, can be used. Within the framework of mixing processes, any color shade can be established both for small and large amounts selectively for glass beads, or glass granulates.

The firing of metal oxide colors onto the surface of the glass particles, which is done within the framework of the invention, can be done selectively in an oxidizing or reducing atmosphere, yielding either transparent colors or metallic surfaces. The latter are important for desired heat or light reflection, and it should be mentioned that in a reducing atmosphere, special metal vapor deposition can be abandoned.

In the case of using copper oxide colors in an oxidizing atmosphere, blue and green colors result, while in a reducing atmosphere, yellow and red colors arise. When using bismuth oxide colors, on the other hand, in an oxidizing atmosphere, silvery colors arise. While using bismuth oxide in a reducing atmosphere, lemon yellow or gold colors are formed. Finally, when using silver oxide colors and salts, in the case of an oxidizing atmosphere, silvery surfaces can be achieved, and

while in a reducing atmosphere, yellow or lemon colors are formed.

Within the framework of the process, colored glass granulate provided with a colored outside layer can be used either as the raw material for Pate-de-Verre operations or a subsequent forming process can be carried out in which colored glass beads are produced from coated colored glass granulates. Forming of glass beads from originally colorless glass granulates, can be done selectively before or after application of an outer colored layer.

2. Application of one layer of glass beads or colored glass granulates on the surface of a carrier material.

In this case, the raw material can be any carrier material, for example, in the form of already fired or vitrified porcelain, stoneware, ceramic tiles, glass plates, glass films or bodies formed from these materials. These bodies can be vitrified brick, ceramic elements, tessellae, vessels, vases or any other bodies of this type.

Within the framework of the invention, a thin layer of a low melting silicate flux, or enamel, is applied to this carrier material either by means of a brush, a screen printing process, by spraying on, or by rolling on. Since these materials are generally powdered, they should be mixed with a liquid wetting agent, for example, in the form of an easily gasifying screen printing oil, so that in this way a viscous mass, which can be applied results. The low melting glass flux is chosen such that its melting point is below the temperature range between 540°C and 800°C, preferably below the temperature range between 560°C and 660°C. It can be for example a lead borosilicate, a sodium borosilicate, a fluoroborosilicate or special mixtures of these substances.

The carrier material coated with this low melting flux is subsequently provided with a single layer of small glass particles or glass granulates, the diameter of these glass

particles being in the range between 0.3 and 4 mm, or 0.1 and 2.3 mm. The application of these glass particles can be done either by immersion in a container filled with glass particles or within the framework of a sprinkling process carried out in the oblique position, in which excess glass particles roll off. The carrier material coated with a layer of glass particles is then placed in a corresponding furnace and heated to a temperature in the range between 540°C and 800°C, preferably in the range between 560°C and 660°C, the low melting flux being caused to melt. In doing so it can preferably be a tunnel kiln through which the coated carrier material is continually routed by a conveyor means.

After the cooling process, a very strong connection between the carrier material and the applied glass particles arises. The thickness of the applied flux layer should be chosen such that after the melting process, the applied glass particles are embedded in the layer of the low melting flux, in the range between one third and one half of the diameter.

To achieve special optical effects, the low melting glass flux, or the glass particles, can be selectively colored as desired. With respect to the application of differently colored glass particles, correspondingly formed templates can be used.

In the corresponding manner, metallic surfaces can be provided with a layer of colored or uncolored glass particles. In particular, small glass beads have the property that they act as strongly reflect light, so that in this way light-reflecting surfaces are produced. In doing so, for example, the body surfaces of motor vehicles are especially well suited, by which it is possible to better recognize these vehicles even under conditions of poor visibility, for example, in fog. The same of course applies to any other craft, such as ships and aircraft, with surfaces under certain circumstances which can be influenced by the grainy structure of the glass beads, such that reduced frictional resistance within fluid media results. For stationary

metallic surface, for example, the outside metallic facades of tall buildings, or in crash barriers on highways, it can be feasible, if they are provided with light-reflecting surfaces.

Within the framework of the invention, a ceramic fabric is also suitable as the carrier layer, in which the warp and weft threads are preferably looped. In this way, a very durable clothing, or tent fabric, is formed which as a result of its fire resistance and good reflection properties seems especially well suited especially for use in tropical and subtropical environments against strong external incident solar radiation. These light reflecting fabrics can also be used for hanging from ceilings, or as theater curtains.

3. <u>Joining a large number of small glass particles among one another</u>

Either glass beads or glass granulates can be used as the raw material for producing porous glass blocks. The glass granulates, are preferably granulates formed by the mechanical crushing of scrap glass, with the aid of screening glass particles with a grain size as uniform as possible being formed. In this case, glass granulates are used which have a uniform grain size between 0.3 and 4 mm. The glass beads can be spherical glass elements which have a diameter as uniform as possible, in the range between 0.1 and 2.3 mm.

The glass particles used to produce the respective glass blocks, are uniformly wetted within a suitable mixing device with an adhesive which gasifies without residue, for example, crystal ice cement 33 from Hereus. But likewise, an aqueous fluorine solidum boric acid solution, or a glaze binder of cellulose derivatives, or hydrophilic screen printing media which burn off without residue, can be used for this purpose.

Subsequently, 2 to 9% by weight, preferably 3 to 5% by weight, of a low melting silicate flux, or enamel in powder form, can be added, this flux consisting, for example, of lead borosilicate, sodium borosilicate, fluoroborosilicate or mixtures

thereof. Within a mixing device, this mixing process is continued until the glass particles are uniformly coated with this low melting silicate flux, or enamel.

The moldable mass produced in this way, is then formed into relief plates, glass blocks, wall panels, cladding panels, and the like, and is heated inside a corresponding furnace, preferably a tunnel kiln, to a temperature in the range between 540°C and 800°C, preferably in the range between 560°C and 660°C. Here the low melting silicate flux, or enamel, is caused to melt so that after cooling, between the individual glass particles there form bridges which impart the required mechanical strength to the respective glass component. The contact bridges, which have been formed, have sufficient elasticity so that even glass particles with different coefficients of thermal expansion can be joined to one another without flaws being formed within the glass component during temperature fluctuations, cooling processes, and the like. In spite of the different coefficients of thermal expansion of the glass particles used, glass blocks which are stress-free can be produced in this way. Since in these laminated materials, the mutual contact surfaces, between the glass particles, have diameters which must necessarily be less than 0.6 mm, in this way the thermal shock limit of the glass is not reached, so that temperature-caused breaks do not occur. Remaining residual stresses are conversely reduced via the existing heat conduction.

Since the individual glass particles are joined to one another only in the area of their points of mutual contact, a glass block is formed which has a relatively high porosity with low weight. When using glass beads as the raw material, glass blocks form with a specific weight of roughly 1.35, while when using glass granulate glass blocks are formed with a specific weight of roughly 1.25.

Compared to glass blocks of glass granulate, glass blocks of glass beads are distinguished by the fact that due to the exactly stipulated glass bead size both the pore size and

also the pore density can be very accurately set. In addition, the glass beads present within the respective glass blocks, especially in the surface area, cause strong light reflection of the incident light so that these glass blocks are especially well suited as decorative wall elements. In contrast, glass blocks produced from glass granulate exhibit a weakly sparkling effect which is caused by the different light reflection on the melted corners, edges and surfaces of the glass granulate used.

When using optically transparent glass particles and a likewise transparent low melting silicate flux, glass components are formed which at a thickness of roughly 5 cm have transparency of roughly 10%.

Colored glass blocks on the other hand can be produced by colored glass particles or correspondingly colored glass flux. In doing so, its seems plausible that coloring of the silicate flux or enamel represents the economical approach as a result of the much smaller amounts.

The glass components produced within the framework of this invention thus have the following advantages:

1. Compared to other glass laminate elements, they have a relatively low specific weight as a result of the existing pores.

2. Depending on the choice of glass particles used, the porosity of the glass block as claimed in the invention can be set differently so that in this way a certain breathability can be achieved.

3. To achieve different colorations, the most varied types of glass particles can be used without stress problems arising as a result of the different coefficients of thermal expansion.

4. Compared to solid glass elements the glass blocks as claimed in the invention are largely insensitive to thermal shock. The pertinent glass blocks have high thermal stability, according to which the surfaces of the glass blocks can be heated to above 800°C. Based on the air bubble inclusions overly fast

fusion of the glass particles together which are present within the glass blocks is prevented, even if fusion of the surfaces of the glass particles together takes place by the action of heat. If monoaluminum phosphate or ammonium or boron potassium compounds are additionally added to the glass block, nitrogen or expanding foams which prevent destruction by fire for hours develop within the glass block.

5. Furthermore, the glass blocks as claimed in the invention can also be statically loaded on a conditional basis, their being similar to conglomerate rock in their structure. The static loading capacity can be further increased by building up the connecting bridges using fluorosodium borosilicates. An increase of the static loading capacity however also arises by use of glass particle mixes of the same glass composition, or when using glass particles with highly varying grain size. For nonuniform loading, extensive load compensation is achieved via the existing contact bridges between the individual glass particles.

6. Glass blocks can be produced from the most varied scrap glass and require only additives in amounts between 2 and 9% by weight, preferably 3 and 5% by weight, so that these glass blocks can be produced very economically.

7. Compared to newly molten glass, the glass blocks in the invention can be produced with very low power consumption. The agglomeration time, for up to 60 mm thick plates, is roughly 30 minutes, while the cooling phase using capsule cooling without an energy supply, or by applying ceramic fiber mats, can be carried out within 90 minutes.

8. The resulting transparency of the glass blocks is reduced by the fusing together of glass particles with increasing wall thickness and color intensity. At temperatures of 750°C, the transparency can be increased again, the properties of the glass component being changed by the overall sintering of the mixture. In this way, a closed glass block with existing air inclusions and increased internal stresses is formed.

The glass components as embodied by the invention can be used as plates, relief panels, glass blocks, wall linings, cladding panels, decorative articles and many other applications. The glass components can be produced very economically, production costs amounting to roughly 650.00 DM per ton when using scrap glass granulate.

If the pasty mass consisting of glass particles, low-melting flux and liquid wetting agents, before the burning process, is placed in the intermediate space between two flat glass plates and then heat treatment is done, very effective heat-insulating panes can be produced in this way.